

## Determination of volatile organic compounds in river water by solid phase extraction and gas chromatography

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**Abstract:** A simple, rapid, and reproducible method is described employing solid-phase extraction (SPE) using dichloromethane followed by gas chromatography (GC) with flame ionization detection (FID) for determination of volatile organic compound (VOC) from the Buriganga River water of Bangladesh. The method was applied to detect the benzene, toluene, ethylbenzene, xylene and cumene (BTEXC) in the sample collected from the surface or 15 cm depth of water. Two-hundred ml of *n*-hexane-pretreated and filtered water samples were applied directly to a C<sub>18</sub> SPE column. BTEXC were extracted with dichloromethane and average concentrations were obtained as 0.104 to 0.372 µg/ml. The highest concentration of benzene was found as 0.372 µg/ml with a relative standard deviation (RSD) of 6.2%, and cumene was not detected. Factors influencing SPE e.g., adsorbent types, sample load volume, eluting solvent, headspace and temperatures, were investigated. A cartridge containing a C<sub>18</sub> adsorbent and using dichloromethane gave better performance for extraction of BTEXC from water. Average recoveries exceeding 90% could be achieved for cumene at 4°C with a 2.7% RSD.

**Keywords:** solid-phase extraction; river water; environmental analysis; VOC recoveries

### Introduction

Volatile organic compounds (VOC), e.g., benzene, toluene, ethylbenzene, xylene and cumene (BTEXC) are important environmental contaminants because of their high toxicity and widespread occurrence. They are present in aviation fuel (gasoline) and are widely used as industrial solvents and raw materials for production of different commodities (Klist, 1993). Benzene, toluene and ethylbenzene are among compounds designated "priority pollutants" by the US EPA, and action and risk levels of benzene, toluene, ethylbenzene, and xylene are described in Dutch Government quality standards for assessment of soil and water contamination (EQSSW, 1991). Determination of BTEXC in environmental matrices is difficult because of their trace-level presence and losses incurred during sample handling, extraction etc. Recently there has been considerable interest in the development of SPE columns for clean-up, extraction, and pre-concentration of liquid samples (Berrueta, 1995). SPE applications are found in different environmental areas such as soils and sediments (Zhang, 1995), industrial effluents (Deans, 1993) and water samples (Saner, 1979; Auther, 1992; Zhang, 1993). SPE has been used for extraction of BTEXC (Meney, 1998) and sulfur based-VOC (Ojala, 1997) from soils and water, respectively. A few SPE applications have also appeared for VOC components in BTEXC analysis of water samples; a cartridge containing C<sub>18</sub> adsorbent was used to extract BTEX from

industrial effluents (Deans, 1993) and benzene and toluene from sea-water (Saner, 1979). Although the solid phase micro-extraction (SPME) was also applied for isolation of BTEX from water samples either by direct adsorption from the liquid (Auther, 1992) or via headspace sampling (Zhang, 1993), the limitation of SPME for quantitation of sulfur based-VOC has been reported (Murray, 2001). The VOCs analyzed from air and water samples by open-tubular, wall-coated columns (Tan, 2000), solvent trapping (Stone, 2000) and semi-VOC from air by atmospheric pressure chemical ionization mass spectrometry (Charles, 2001) were also described.

Buriganga River water is important because it flows through the capital of Bangladesh and has an enormous impact on socio-economic development of the country, especially industrial and shipping-marine activities. Tanker-washing sewage, shipping scrap particles and oil spillage are common features on the river at different ghats (marine terminals). As a result, the water is continually polluted by various organic compounds especially hydrocarbons. In addition, aromatic solvents are increasingly used in industry (Klist, 1993) and the wastes are sometimes disposed of in the aquatic environment, which becomes increasingly contaminated. To monitor contaminants, we determined the concentrations of normal saturated- and polycyclic aromatic hydrocarbons in Buriganga River water (Mottaleb, 1999c; 2003) and pesticides in soil (Mottaleb, 1999b) by GC, using liquid-liquid extraction and SPE methods. The anionic

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detergents were characterized in river water by chromatographic and spectroscopic methods (Mottaleb, 1999a). The present paper describes concentration levels of VOCs such as benzene, toluene, ethylbenzene, xylene and cumene in water samples collected at two depths from the Sadarghat, one of the biggest marine terminals, on the Buriganga River. Also discussed are recoveries of BTEXC using different adsorbents for SPE columns and factors influencing SPE adsorption, such as, sample load volume, eluting solvent, headspace and temperatures, and so on.

## 1 Experimental

### 1.1 Apparatus and reagents

A Varian gas chromatograph, Model 3300, equipped with flame ionization detector (FID) was used in this study. A DB-1 fused-silica mega-bore, analytical column (15 m × 0.53 mm i. d., 1.5 μm thickness) and phenyl-methyl deactivated guard column were used. An integrator, Varian Model 4290, gave the peak area and retention time of the peaks separated by GC-FID. Methanol (HPLC grade), hexane, dichloromethane and chloroform were obtained from Merck Ltd. (Germany). VOCs and internal standards were purchased from Sigma Chemicals Ltd., USA. C<sub>18</sub>, C<sub>8</sub> and phenyl (PH) (500 mg, 3 ml) SPE cartridges were obtained from the Supelco Ltd.

### 1.2 Stock and working standard solutions

#### 1.2.1 Stock solution

An aliquot (10 μl) of each of the BTEXC constituents and internal standard dichlorobenzene (DCB) were dissolved in 100 ml dichloromethane. Concentrations of BTEXC components corresponded to 87.7, 86.7, 86.7, 86.1, 86.1 μg/ml, respectively and the concentration of DCB corresponded to 130.5 μg/ml.

#### 1.2.2 Working standard solutions

Four standard solutions were made for measuring the linearity of GC response. The concentrations of the standard solutions are shown in Table 1.

**Table 1** Concentration of BTEXC standard solution used for GC optimization

Solutions	Concentration of BTEXC standard solution, μg/ml				
	Benzene	Toluene	Ethylbenzene	Xylene	Cumene
Standard 1	8.77	8.67	8.67	8.61	8.61
Standard 2	17.14	17.34	17.35	17.22	17.22
Standard 3	26.31	26.01	26.01	25.83	25.83
Standard 4	35.08	34.68	3.68	34.44	34.44

### 1.3 Collection of river water samples

Contaminated water samples were collected in 1 L dark glass bottles on September 21, 1999 from the Sadarghat. A map of the Buriganga River and the location of the Sadarghat area are reported (Mottaleb, 1999c). Cleaned bottles were rinsed with sample water prior to sample collection. Ten-liter samples were collected at the surface and ten samples were also collected at a depth of 15 cm. The distance of the

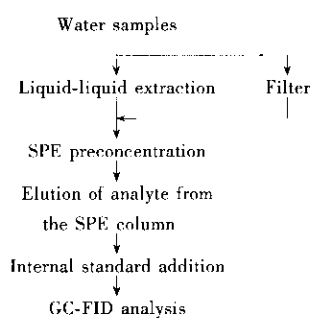
sample collection point from the river bank was about 200 m. Method development work was carried out using double-distilled water containing BTEXC at the same concentrations as those found in the river water. The synthetic samples were prepared daily at a pH of 6.5.

### 1.4 Extraction of VOC from synthetic and river water samples

A 10 ml volume of synthetic sample was extracted with 10 ml of hexane in a 30 ml vial; the layers were allowed to separate. Prior to SPE work, 2 to 4 ml of the organic layer were removed and stored in a sealed glass vial at 4°C. The extraction of river water sample was carried out according to the reported method (Mottaleb, 1999c; 2003). Each (500 ml) water sample was shaken for 30 min with 50 ml of hexane at 4°C. The aqueous layer was separated and extracted again with 25 ml hexane. The combined extracts were then stored at 4°C for SPE. Prior to direct use of the water sample in SPE, the sample (200 ml) was filtered by a 0.45 μm nylon membrane.

### 1.5 Solid-phase extraction

The column was activated with 3 ml 50% methanol and pre-equilibrated with 3 ml 1% methanol. Synthetic (2 ml) or river water (100 ml) sample was loaded on the column at 3 m/min. Elution was carried out with 2 portion of 2 ml aqueous 1% methanol. Finally, solutes were eluted with two aliquots of 2 ml dichloromethane. Passing samples through a dryer containing sodium sulfate eliminated traces of water only. Similar elution profiles were obtained for the recovery experiments. The DCB (200 μl or 5%) was added as the internal standard prior to GC analysis. A schematic representation of experimental procedure is shown in Fig. 1.



**Fig. 1** A simplified schematic representation of the experimental procedure

### 1.6 Calculation of response factor and concentration of components

The relative response factor of a component ( $R_f$ ) to the internal standard of DCB is given by:

$$R_f = \frac{C_{DCB}}{A_{DCB}} \times \frac{A_c}{C_c}$$

Where,  $C_{DCB}$  and  $C_c$  represent the concentrations of DCB and component analyte, respectively in terms of μg/ml. The terms  $A_{DCB}$  and  $A_c$  indicate the peak area counts from integrator for DCB and component analyte, respectively. Response factors for all components were calculated as above and the

concentration of each component ( $C_c$ ) calculated as follows:

$$C_c = \frac{A_c}{A_{DCB}} \times \frac{C_{DCB}}{R_F}$$

## 2 Results and discussion

### 2.1 GC optimization

The GC-FID system used was optimized before the VOC measurement. Separations were achieved with different temperature programs. A good separation of individual BTEXC constituents including DCB was obtained. Fig. 2 is a GC-FID chromatogram of the standard solution of BTEXC components showing that the components and DCB were well resolved. The linearity of the detector response was also demonstrated by injecting the working standard solutions into the GC-FID instrument. Fig. 3 depicts the calibration graph of peak area versus concentration. The FID gave good linearity of response for detection of each of the BTEXC constituents. Hence, it was decided, that the above conditions could be used for determination of BTEXC from the river water samples.

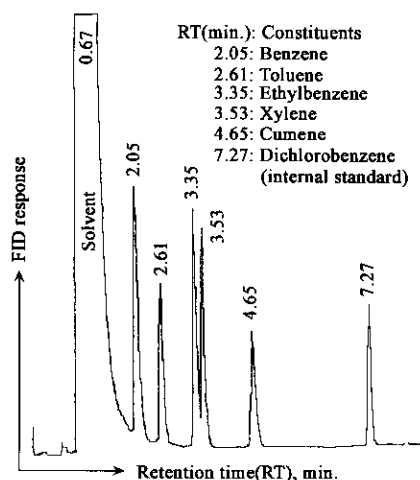


Fig. 2 GC-FID detection chromatogram for standard solution of BTEXC and dichlorobenzene

Conditions: gas flow rates:  $N_2$  (carrier gas) 4 ml/min,  $H_2$  33 ml/min, air 330 ml/min, detector temperature 180°C, injector temperature 180°C, mega-bore DB-1 fused silica column (15 m  $\times$  0.53 mm i. d., 1.5  $\mu$ m thickness), oven temperature program: 35°C for 5 min, to 70°C at 5°C/min, to 180°C at 15°C/min and hold 10 min at 180°C and sample injection 1  $\mu$ l

### 2.2 Presence of VOC in water samples

Table 2 summarizes the concentration of BTEXC in the river water samples analyzed by SPE-GC-FID. The presence of ethylbenzene, xylene and cumene were not detected using the experimental conditions described above, although trace levels of benzene and toluene were found. To detect the other constituents of the BTEXC family, an increased volume of 200 ml of water sample was directly applied to the SPE at 4°C. An appreciable amount of benzene and toluene, including trace levels of ethylbenzene and xylene, were detected in the river water sample. The concentrations of BTEX in the water sample were found from the range of

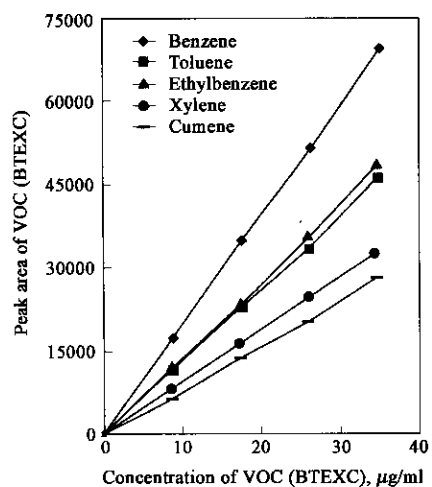


Fig. 3 Calibration curve for optimization of GC-FID system for analysis of BTEXC in the Buriganga river water

Concentration of injected BTEXC solution (please see experimental, preparation of stock and working standard solutions). Operating conditions are the same as in Fig. 2

0.124 to 0.350  $\mu$ g/ml and 0.104 to 0.372  $\mu$ g/ml at surface (0 cm) and 15 cm depths, respectively, with a RSD value around or less than 10%. Samples collected from both depths gave higher concentration for benzene. The cumene was never detected. This was quite reasonable and expected since cumene is easily oxidized to produce phenol and acetone. Fig. 4 shows a representative GC-FID chromatogram of the river water samples. Chromatograms in Fig. 4a and Fig. 4b corresponded to surface and 15 cm depth of water samples, collected from the Buriganga River. These were obtained when 2  $\mu$ l sample was injected into the GC instrument. A similar chromatographic elution pattern of BTEX components was found to observe between the standard (Fig. 2) and samples (Fig. 4) solution chromatograms. Blank experiments were performed prior to standard and sample solutions injection on regular basis.

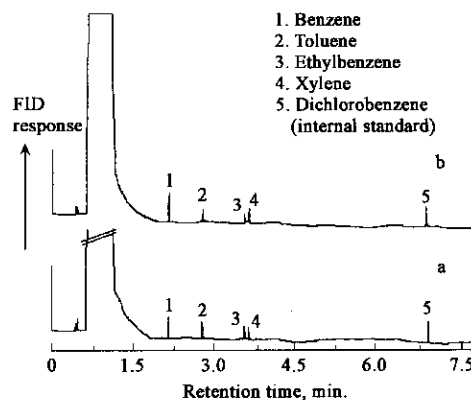


Fig. 4 GC-FID chromatograms for the river water samples. For (a), water was collected from surface, and for (b), water was collected from 15 cm depth. Operating conditions are the same as in Fig. 2

**Table 2** SPE of river water samples at 4°C (C<sub>18</sub> column, sample volume 200 ml)

Analytes	Concentration of BTEXC component in river water, µg/ml					
	0 cm depth			15 cm depth		
	Average conc.	SD*	RSD*, %	Average conc.	SD*	RSD*, %
Benzene	0.350	± 0.034	9.8	0.372	± 0.023	6.2
Toluene	0.234	± 0.024	10.3	0.167	± 0.017	10.2
Ethylbenzene	0.145	± 0.014	9.7	0.104	± 0.011	10.6
Xylene	0.124	± 0.011	8.9	0.144	± 0.014	9.7
Cumene	-	-	-	-	-	-

Notes: SD\* represents standard deviation and were calculated from each of four measurements; RSD\* means relative standard deviation

### 2.3 Selection of adsorbents and eluting solvent

To select the suitability of adsorbents and eluting solvents, the percentage recovery of BTEXC constituents was

**Table 3** Recovery of BTEXC from different SPE columns eluted with CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub> at temperature of 4°C

Solvents	SPE columns	Recoveries (%) ± standard deviation (SD*)				
		Benzene	Toluene	Ethylbenzene	Xylene	Cumene
CH <sub>2</sub> Cl <sub>2</sub>	C <sub>18</sub>	76.0 ± 2.5	80.5 ± 2.5	83.7 ± 3.5	87.1 ± 4.0	90.3 ± 3.3
	C <sub>8</sub>	70.0 ± 3.5	68.3 ± 2.0	74.6 ± 3.5	83.7 ± 1.5	79.6 ± 1.4
	PH	73.0 ± 1.5	77.8 ± 3.5	70.4 ± 4.0	76.3 ± 1.5	82.5 ± 2.3
CHCl <sub>3</sub>	C <sub>18</sub>	74.0 ± 3.0	78.0 ± 2.5	80.0 ± 2.0	84.0 ± 3.0	87.0 ± 4.0
	C <sub>8</sub>	69.0 ± 3.5	67.0 ± 2.5	72.0 ± 3.0	80.0 ± 2.5	77.0 ± 3.0
	PH	71.2 ± 3.0	76.0 ± 3.0	69.0 ± 4.0	75.0 ± 3.0	78.0 ± 2.5

Notes: SD\* values were calculated from each of five measurements

### 2.4 Effect of sample load volume

The effect of sample volume on SPE recovery is one of the most important factors as SPE performance is affected by the amount of sample volume loaded on a particular column (Deans, 1993; Meney, 1998). The break-through volume of a C<sub>18</sub> column (500 mg, 3 ml capacity) was determined by passing a number of VOC standard solutions to a volume up to 500 ml. Known masses of the analytes were introduced. There were no appreciable changes in the recovery rates up to a sample volume of 400 ml. The percentage recovery of benzene and toluene decreases more rapidly than ethylbenzene, xylene and cumene. This observation confirms the fact that ethylbenzene, xylene and cumene possess higher breakthrough volumes than benzene and toluene (Fig. 5). Similar break-through volume curves were obtained for C<sub>8</sub> and phenyl substituted SPE columns. These are not shown.

### 2.5 Factors affecting the SPE performance investigations

#### 2.5.1 Temperature

To investigate the effect of temperature on SPE performance, a cartridge containing C<sub>18</sub> material was employed with CH<sub>2</sub>Cl<sub>2</sub> solvent at 20°C and 4°C. An effect of temperature on SPE recovery of BTEXC constituents was found to occur (Table 4). It has been observed that both liquid-liquid and solid-phase extractions provided slightly better recoveries when experiments were carried out at 4°C. The RSD was calculated for each of BTEXC constituents and temperatures. At 20°C, the RSD of recoveries were between

investigated using C<sub>18</sub>, C<sub>8</sub> and PH cartridges with CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub> solvents. The recoveries obtained when 2 ml of standard VOC solutions were passed through different SPE columns and eluted with two portions of 2 ml of dichloromethane or chloroform at 4°C and at least five experiments were performed for each measurement. The recovery results are presented in Table 3. The extractions were performed simultaneously for each solvent. Higher recoveries were obtained for xylene and cumene. This may be due to less evaporative loss of the two components because of their higher boiling point. Moreover, in comparison between CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub> solvents, it was observed that slightly better recoveries were obtained when CH<sub>2</sub>Cl<sub>2</sub> was used as eluting solvent (Table 3).

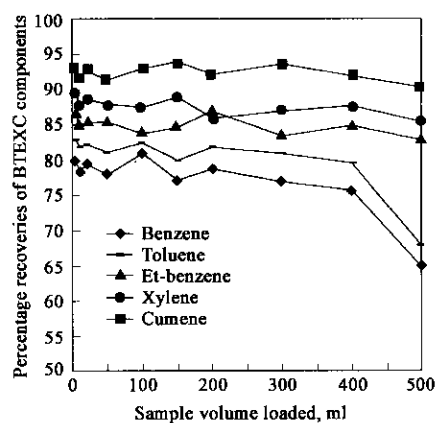


Fig. 5 Effect of sample load volume on the recoveries of BTEXC constituents with C<sub>18</sub> SPE column using dichloromethane solvent

3.3% and 4.0%; however at 4°C, the slightly improved recoveries of constituents were achieved with RSD values of 2.7 to 3.5%.

#### 2.5.2 Headspace

In order to investigate the effect of headspace, the recovery experiments for each of the BTEXC components were performed using C<sub>18</sub> column in an environment of a temperature of 4°C. This temperature provided recoveries of 79% to 91% of the constituents (Table 4). The parallel extraction of the components with and without headspace was performed. The results are presented Table 5. It can be seen that the incurred losses of the BTEXC constituents occurred in the range of 8.9% to 11.8% due to allowing the headspace. Since trace levels of BTEXC components could be

found in real samples, so over 9% losses are quite significant. Thus it was concluded that the existence of headspace increases the evaporative losses. This study was conducted allowing no headspace at 4°C.

**Table 4** Effect of temperature on recovery of BTEXC with CH<sub>2</sub>Cl<sub>2</sub> using C<sub>18</sub> cartridge

Analytes	Extraction with C <sub>18</sub> cartridge					
	At a temperature of 20°C			At a temperature of 4°C		
	Recovery, %	SD *	RSD *, %	Recovery, %	SD *	RSD *, %
Benzene	76	± 3.0	3.9	79	± 2.8	3.5
Toluene	82	± 2.9	3.5	86	± 2.5	2.9
Ethylbenzene	84	± 3.3	3.9	91	± 3.2	3.5
Xylene	87	± 3.5	4.0	88	± 2.7	3.1
Cumene	89	± 2.9	3.3	91	± 2.5	2.7

Notes: SD \* represents standard deviation and were calculated from each of five measurements; RSD \* means relative standard deviation

**Table 5** Effect of headspace on the recovery of BTEXC with CH<sub>2</sub>Cl<sub>2</sub> using C<sub>18</sub> cartridge at 4°C

Analytes	Headspace		No headspace		Recovery difference, %
	Recovery, %	SD *	Recovery, %	SD *	
Benzene	67.0	± 2.0	76.0	± 3.0	11.8
Toluene	72.0	± 3.5	81.0	± 2.5	11.1
Ethylbenzene	74.0	± 3.5	84.0	± 2.5	11.9
Xylene	79.0	± 2.7	87.0	± 4.0	9.2
Cumene	82.0	± 2.8	90.0	± 3.5	8.9

Notes: SD \* represents standard deviation and were calculated from each of five measurements

### 3 Conclusions

A simple and less expensive method has been demonstrated for detection of BTEXC from river water sample by GC-FID. The water sample from the surface (0 cm depth) found the concentrations of BTEX as 0.350, 0.234, 0.145, and 0.124 µg/ml, respectively. Samples collected from 15 cm depth gave concentrations of BTEX as 0.372, 0.167, 0.104, and 0.144 µg/ml, respectively. Recoveries of BTEXC employing SPE columns containing C<sub>18</sub>, C<sub>8</sub>, and phenyl functionalities using CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>4</sub> eluents were not significantly different. An operating temperature, 4°C, showed slightly better recovery rates compared to 20°C. Average recoveries exceeding 90% could be achieved for cumene at 4°C with a 2.7% RSD. Experiments with and without headspace suggested that over 9%-improved recoveries rate could achievable with allowing no headspace at 4°C for BTEXC analysis.

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### References:

- Auther C L, Pawliszyn J, Belardi P R, 1992. Environmental analysis of organic compounds in water using solid phase microextraction [J]. *J High Resol Chromatogr*, 15: 741—744.
- Berrueta I A, Gallo B, Vicente F, 1995. A review of solid phase extraction: basic principle and new development [J]. *Chromatographia*, 40: 474—483.
- Charles L, Riter L S, Cooks R G, 2001. Direct analysis of semivolatile organic compounds in air by atmospheric pressure chemical ionization mass spectrometry [J]. *Anal Chem*, 7: 5061—5065.
- Deans I S, Davidson C M, Littlejohn D *et al.*, 1993. Factors affecting the solid phase extraction of semi-volatiles organic pollutants from acidic industrial effluent for analysis by GC [J]. *Analyst*, 118: 1375—1382.
- EQSSW (Environmental Quality Standards for Soil and Water), 1991. Physical planning and environment [M]. Leidschendam: Netherlands Ministry of Housing.
- Klist J J G, 1993. In: Chemistry and analysis of VOCs in the environment (Bloemen H. J. T. and Burn J. ed.) [M]. Glasgow.
- Meney K M, Davidson C M, Littlejohn D, 1998. Use of solid phase extraction in the determination of benzene, toluene, ethylbenzene, xylene and cumene in spiked soil and investigation of soil spiking methods [J]. *Analyst*, 123: 195—200.
- Mottaleb M A, 1999a. Development of HPLC method for analysis of linear alkylbenzene sulphonates and detection by UV and FTIR spectroscopy using a thermospray interface [J]. *Mikrochim Acta*, 132: 31—39.
- Mottaleb M A, Abedin M Z, 1999b. Determination of chlorinated pesticides from soil by solid phase extraction-gas chromatography [J]. *Anal Sci*, 15: 283—288.
- Mottaleb M A, Ferdous M, Islam M S *et al.*, 1999c. Determination of normal saturated hydrocarbons in Buriganga River water of Bangladesh by gas liquid chromatography [J]. *Anal Sci*, 15: 995—1000.
- Mottaleb M A, Sarma D K, Sultana S *et al.*, 2003. Determination of normal saturated- and polycyclic aromatic hydrocarbons in the river water Bangladesh by liquid-liquid extraction and gas liquid chromatography [J]. *Bull Kor Chem Soc*, 24: 99—105.
- Murray R A, 2001. Limitations to the use of solid phase microextraction for quantitation of mixtures of volatile organic sulfur compounds [J]. *Anal Chem*, 73: 1646—1649.
- Ojala M, Ketola R, Mansikki T *et al.*, 1997. Detection of volatile organic sulfur compounds in water by headspace gas chromatography and membrane inlet mass spectrometry [J]. *J High Resol Chromatogr*, 20: 165—169.
- Saner W A, Djadamec J R, Sager R W *et al.*, 1979. Trace enrichment with hand-packed CO: PELL ODS guard columns and SEP-PAK C<sub>18</sub> cartridge [J]. *Anal Chem*, 51: 2180—2188.
- Stone M A, Taylor L T, 2000. Improved solvent trapping of volatiles in supercritical fluid extraction by pressurizing the collection vial [J]. *Anal Chem*, 72: 1268—1274.
- Tan B C D, Marriott P J, Lee H K *et al.*, 2000. Sorption of volatile organics from water using open tubular, wall coated capillary column [J]. *Analyst*, 125: 469—475.
- Zhang Z, Pawliszyn J, 1993. Headspace solid phase microextraction [J]. *Anal Chem*, 65: 1843—1852.
- Zhang Z, Pawliszyn J, 1995. Quantitative extraction using an internally cooled solid phase microextraction device [J]. *Anal Chem*, 67: 34—43.

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